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(54) WROUGHT LEAD-CALCIUM AND LEAD-CALCIUM-TIN ALLOYS

We, St. Joe Minerals Corpora-TION, a corporation organised and existing under the laws of the State of New York, of 250 Park Avenue, New York, New York, 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the fol-10 lowing statement:-

The present invention relates to a process for the preparation of wrought lead-calcium and lead-calcium-tin alloys which have tensile strength stability at room temperature

15 and to alloys produced thereby.

Lead containing alloys are useful in a variety of fields, such as in the construction of batteries. Alloys of lead, however, have physical properties which are somewhat deficient in ragard to strength, strength stability at room temperature, heat stability and stress-rupture or creep resistance.

It is an object of the present invention to provide wrought alloys of lead having ten-25 sile strength stability at room temperature and according to certain embodiments of the invention having improved strength, heat stability and stress-rupture or creep resist-

Our prior Application No. 2474/71 (Serial No. 1,338,823) relates to a process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises casting an alloy consisting of from 0.02% to 0.1% by weight of calcium and the balance substantially lead; and working the casting at room temperature at a time within 8 hours from casting.

The said prior application also relates to 40 a process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises casting an alloy consisting of from 0.02% to 0.1% by weight of calcium, tin in an amount 45 such that the tin to calcium weight ratio is from 5:1 to 10:1 and the absolute tin content is from 0.3% to 3.0% by weight, and the balance substantially lead; and working the casting at room temperature at a time within 48 hours from casting.

(11)

The said prior application further relates to a process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises casting an alloy consisting of from 0.02 to 0.1% by weight of calcium, tin in an amount such that the tin to calcium weight ratio is from more than 10:1 to 150:1 and the absolute tin content is from 0.3% to 3.0% by weight and the balance substantially lead; and working the casting at room temperature at a

time within 7 days from casting.

The present invention relates to a modificaton of the process of our said prior application in that it has now been found that if the alloys are aged after casting the same desirable properties can still be produced provided that the aged workpiece produced is heated at a temperature and for a time sufficient to place the calcium in solid solution in the lead, the work piece is cooled to ambient temperature to form a super-saturated solid solution of the calcium in the lead and then cold worked after cooling within the time periods defined according to our

prior application.

Thus in general, the present invention provides for the production of stable wrought alloys of lead by casting a lead-containing alloy having a defined calcium content, and preferably defined relative and absolute tin contents, to provide an aged workpiece, heating the aged workpiece at a temperature and for a time sufficient to place the calcium in solid solution in the lead, cooling the workpiece to ambient temperature to form a super-saturated solid solution of the calcium in the lead and thereafter cold working the workpiece within a defined limited time period from cooling.

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The maximum time period between cooling and working is essential in order to produce wrought lead-calcium alloys and wrought lead-calcium-tin alloys which have tensile strength stability at room temperature, i.e. the wrought alloys produced according to the invention have strengths which are either immediately stable at room temperature ("immediate stability") or which increases gradually with time up to 60-120 days or more and then become stable at room temperature ("long-range stability") as opposed to wrought alloys having strengths at room temperature which decrease with time either immediately or months after working. This time period between cooling and working can be greater as the relative tin to calcium content is increased.

The tin: calcium weight ratio or relative tin content is important in order to produce wrought lead alloys not only having strength stability at room temperature but also having improved strength, heat stability and stressrupture or creep resistance. These latter properties increase and then decrease as the tin to calcium weight ratio increases.

It is also important that the absolute tin content be regulated, particularly so as not to exceed a maximum value, in order to 30 achieve strength stability at room tempera-

More specifically, the present invention provides a process for the preparation of a wrought alloy of lead having tensile strength 35 stability at room temperature which comprises heating an aged workpiece of an alloy consisting of from 0.02% to 0.1% by weight of calcium and the balance substantially lead, the said heating being at a temperature and 40 for a time sufficient to place the calcium in solid solution in the lead; cooling the workpiece to ambient temperature to form a super-saturated solid solution of the calcium in the lead and cold working the workpiece at a time within 8 hours from cooling. It is preferred that the alloy has a calcium content of from 0.06% to 0.09% by weight. In this preferred embodiment, it will be appreciated that as a commercially practical matter, the concentration of calcium may not be precisely controlled, preferred compositions nominally having a 0.06%—0.09% concentration may actually include alloys in which only about 0.05% to about 0.09% calcium is 55 used.

Significant strengthening of the alloy can be achieved by adding tin in an amount such that the tin to calcium weight ratio or relative tin content is from 5:1 to 10:1, and the absolute tin content is from 0.3% to 3.0% by weight and in this case cold working must take place at a time within 48 hours from cooling. It is preferred that the alloy contain tin in an amount such that the tin to calcium weight ratio or relative tin content is from more than 10:1 to 150:1 and more preferably is from 16:1 to 40:1 and the absolute tin content is from 0.3% to 3.0% in which case cold working must take place at a time within 7 days from cooling. Preferably the absolute tin content is from 0.6% to 2.0% by weight of the alloy. Most preferably the tin to calcium weight ratio is about 25:1.

The alloys are cold worked within a particular limited time period after cooling which time period can be increased as the relative tin to calcium content is increased. Thus, the tin-free lead-calcium alloys must be cold worked within 8 hours after cooling. However, the tin-containing lead-calcium alloys having a tin to calcium weight ratio of from 5:1 to 10:1 can be cold worked within 48 hours after cooling and the tin-containing lead-calcium alloys having a tin to calcium weight ratio of from more than 10:1 up to 150:1 can be cold worked within 7 days after cooling. Even with these two types of tin-containing lead-calcium alloys, however, it is preferred that they be cold worked within 8 hours after cooling because of the superior properties obtained thereby.

Conventional batch or continuous metallurgical techniques can be employed in the casting, heating, cooling and cold working operations of the process of the invention. Cold working can include such techniques as rolling, extruding, forging and the like.

While the present invention is not limited to any particular theory, the following is 100 helpful to an understanding thereof.

The lead-calcium and lead-calcium-tin alloy systems produced both according to the present invention and according to our prior Application No. 2474/71 (Serial No. 105 1,338,823) are believed to be strengthened by a process known as "precipitation strengthening". In these alloys calcium is much less soluble in the lead lattice at room temperature than at elevated temperatures. 110 Cooling a casting of a lead-calcium or leadcalcium-tin alloy to ambient temperature in a reasonable amount of time produces a super-saturated solid solution containing substantially more calcium than can normally be 115 dissolved at ambient temperature. With time. the excess calcium precipitates in the lead matrix in the form of an intermetallic compound which strengthens the lead. The rate at which the calcium precipitates depends on 120 the chemical composition of the alloy. Calcium precipitates from the lead-calcium-tinalloy system at a slower rate than it does from the lead-calcium alloy system.

Previously unknown interactions between 125 precipitation and deformation have now been discovered. If a casting is cold worked, prior to precipitation of the excess calcium, the mechanical properties of the cold worked piece will be immediately stable and may 130

even increase in strength with time and then become stable. If, however, the casting is cold worked after substantially all of the excess calcium has precipitated, the mechanical properties will decrease during aging at ambient conditions. The amount of decrease will depend on the chemical composition and the amount of calcium precipitation prior to deformation.

As is well known in the metallurgical arts, cold working involves the mechanical deformation of a work piece at a temperature low enough that dislocations caused by working are retained. By contrast, in hot working the temperature of the work piece is sufficiently high that dislocations caused by working are rapidly dissipated by annealing. The improved properties obtained according to the present invention and the process of our prior Application 2474/71 (Serial No. 1,338,823) depend on an interaction between the dislocations of cold working and the precipitated calcium which gives rise to stable or even improving mechanical properties with age. The best results are obtained if the amount of cold working is equivalent to a deformation of 4/1 or greater (i.e. reducing a $\frac{1}{2}$ " strip by cold rolling to a thickness of $\frac{1}{8}$ " or less). Lesser degrees of improvement are observed, however, even with less extensive cold working.

It will be appreciated from the foregoing that the benefits of cold working can be obtained provided it is carried out within a 35 defined time after casting. This is the subject of our prior Application 2474/71 (Serial No. 1,338,823). However the benefits of cold working are not limited to the cold working of freshly cast lead-calcium-tin alloys. cording to the present invention aged leadcalcium and lead-calcium-tin alloys, even after all of the excess calcium has precipitated, may be restored to a condition permitting working or reworking by heating such pieces to a temperature sufficient to redissolve the precipitated calcium and then cooling again to ambient temperatures. Remelting and recasting is not necessary. This process of restoring lead-calcium and lead-calcium-tin alloys so that they may be cold worked is referred to herein as "solution treatment".

Solution treatment consists of heating a previously aged working piece having an alloy composition of the type described herein to a temperature sufficiently high, and holding the work piece at that temperature for a sufficiently long period of time, so that the calcium re-enters into solid solution in the lead. If the alloy is then cooled to ambient conditions in a reasonable period of time, a super-saturated solid solution containing an excess of calcium, just as in freshly cast material, will be produced and the solution-treated work piece will behave in a manner identical to that of a fresh cast-

As a general guide it is sufficient to heat the work piece to the temperature at which the calcium is soluble in the lead for a reasonable period of time. This may be determined by consulting an appropriate phase diagram, see for example the test Constitu-tion of Binary Alloys by Max Hansen, McGraw-Hill Publishing Co. As a simple guide to determining whether the calcium has been redissolved, the hardness or strength of the solution-treated work piece may be compared with that of a freshly cast alloy of the same composition. Techniques for forming super-saturated solutions of calcium in lead are generally known in the art, see British Patent No. 314,522.

The solution treatment method according to the invention is applicable to work pieces which have been cast and held in storage for a period of time too long to permit hardening by cold working according to our prior Application 2474/71 (Serial No. 1,338,823) and, also to work pieces which may have been cast and previously cold worked and which may have been cast and previously cold worked and which are to be subjected to further cold working, although of an age such that the excess calcium has already precipitated.

In the practice of this invention, the work piece is normally cold worked at an essentially room temperature or the existing ambient temperature of the shop. However, it will be obvious that any process of cold 100 working tends to generate heat and results in raising somewhat the temperature of the work piece. As described herein, when cold working the work piece at room temperature in ambient conditions, no special effort is 105 made or need be made to dissipate the heat generated by cold working. In general the ambient conditions used for the practice of this invention are those normally found in a work shop. All that is required is that the 110 piece after solution treatment be laid in the open where it can cool by natural convection, typically in a period of a few hours or less. After the work piece has reached a temperature at which it can be conveniently 115 handled (typically less than about 135°F.)

cold working can proceed.

For a detailed discussion of the properties of the alloys which can be produced according to the invention reference is made to our 120 prior Application 2474/71 (Serial No. 1,338,823).

The invention is illustrated by the following examples:

Example 1 A lead-0.8% calcium alloy was continuously cast into a billet \(\frac{1}{4}'' \) thick \times 10\(\frac{1}{2}'' \) wide at a temperature of 700°F, and a withdrawal

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speed of 3½ feet per minute to produce a surface suitable for rolling. The alloy was aged for 60 days at room temperature to assure complete precipitation of excess calcium. Two sections of this material were heated to a temperature of 315°C. for 2 cium. hours and subsequently cooled to room temperature. This material was rolled after aging for one hour and after aging for 30 days at room temperature. The rolled material was subsequently aged for up to one year at room temperature and tested at periodic intervals. Fig. 1 shows the aging behaviour of the two rolled materials. The material which was rolled after aging for one hour at room temperature following solution treatment, Curve A¹, had an initial strength of about 5400 psi. and was stable throughout one year of aging. The material aged for 30 days after solution treatment, Curve E¹, had an initial strength of about 7000 psi. and subsequently decreased until after 180 days the material exhibited less strength than that produced by the process of the present invention.

The behaviour of the solution treated material was almost identical to that of a freshly cast billet processed in a similar manner. This can be seen by comparing Curves A¹ and E¹ of Fig. 1 with the curves for Process A and Process E in Fig. 1 of the drawings accompanying our prior Application No. 2474/71 (Serial No. 1,338,823).

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EXAMPLE

A lead-0.065% calcium-1.3% tin alloy was continuously cast, aged and solution treated as described in Example 1. Fig. 2 shows the aging behaviour of the two rolled samples. The sample rolled after aging for one hour at room temeprature following solution treatment, Curve A1, had an intitial strength of about 7200 psi, and during aging reached a strength of 10,500 psi, after 120 days. The sample aged for 30 days at room temperature before rolling (Curve E¹) only reached a maximum strength of 9200 psi. and subsequently lost strength during aging.

The behaviour of the two samples in these examples is directly comparable to that of cast and rolled materials shown in Fig. 3 of the drawings accompanying our prior Application No. 2474/71 (Serial No. 1,338,823). The solution treated material according to the 55 present invention reaches a slightly higher strength than that of the 0.08%-calcium 1.0% tin alloy according to the said prior application because of the higher Sn/Ca ratio of the solution treated material.

WHAT WE CLAIM IS:-

1. A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises heating an aged work piece of an alloy

consisting of from 0.02% to 0.1% by weight of calcium and the balance substantially lead, the said heating being at a temperature and for a time sufficient to place the calcium in solid solution in the lead; cooling the workpiece to ambient temperature to form a super-saturated solid solution of the calcium in the lead; and cold working the work piece at a time within 8 hours from cooling.

2. A process as claimed in claim I wherein the alloy has a calcium content of from

0.06% to 0.09% by weight.

A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises heating an aged work piece of an alloy consisting of from 0.02% to 0.1% by weight of calcium, tin in an amount such that the tin to calcium weight ratio is from 5:1 to 10:1, and the absolute tin content is from 0.3% to 3.0% by weight, and the balance substantially lead, the said heating being at a temperature and for a time sufficient to place the calcium in solid solution in the lead; cooling the work piece to ambient temperature to form a super-saturate solid solution of the calcium in the lead; and cold working the work piece at a time within 48 hours from cooling.

4. A process as claimed in claim 3 wherein the alloy has a calcium content of from

0.06% to 0.09% by weight.

5. A process as claimed in claim 3 or 4 wherein the work piece is cold worked at a time within 8 hours from cooling.

6. A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises heating an aged work piece of an alloy consisting of from 0.02% to 0.1% by 105 weight of calcium, tin in an amount such that the tin to calcium weight ratio is from more than 10:1 to 150:1 and the absolute tin content is from 0.3% to 3.0% by weight, and the balance substantally lead, the said 110 heating being at a temeprature and for a time sufficient to place the calcium in solid solution in the lead; cooling the work piece to ambient temperature to form a supersaturated solid solution of the calcium in the 115 lead; and cold working the work piece at a time within 7 days from cooling.

7. A process as claimed in claim 6 wherein the alloy has a calcium content of from 0.06% to 0.09% by weight.

8. A process as claimed in claim 6 or 7 wherein the tin to calcium weight ratio is from 16:1 to 40:1 and the absolute tin content is from 0.6% to 2.0% by weight.

9. A process as claimed in claim 8 where- 125 in the tin to calcium weight ratio is about 25:1.

A process as claimed in any of claims 10. 6 to 9 wherein the work piece is cold worked at a time within 8 hours from cooling.

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11. A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature as claimed in any of claims 1, 3 or 6 substantially as hereinbefore described with reference to either of the Examples.

12. A wrought alloy of lead having tensile strength stability at room temperature

when prepared by a process as claimed in any of claims 1 to 11.

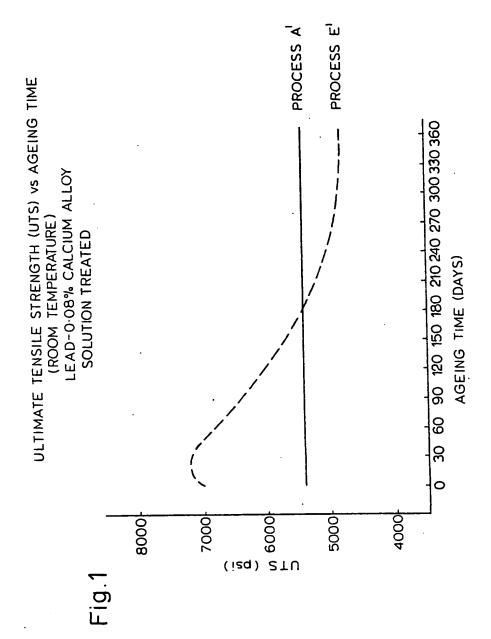
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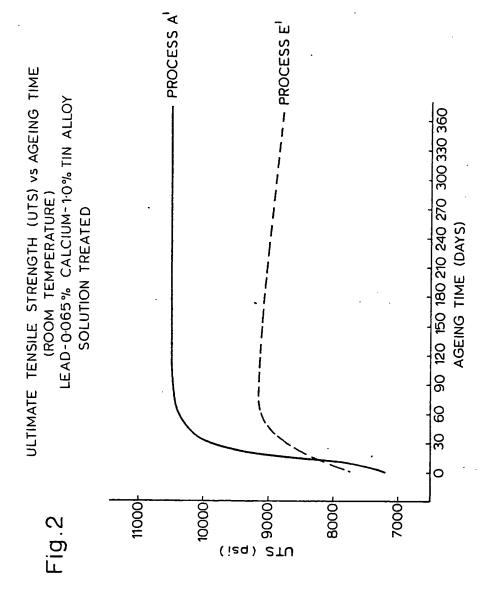
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